Asphaltenes, Waxes, Emulsions, and Oil Suspensions: Inline Particle and Droplet Measurements in Dark Crude Oil

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Abstract

Liquid, solid, and gaseous hydrocarbon pipeline flow is typically a complex multi-phase system comprised of particles and droplets including waxes, asphaltenes, gas hydrates, emulsions, inorganic particles, and bubbles.

Multiphase pipeline flow often occurs under extreme temperature and pressure conditions making offline sampling and analysis difficult or impossible.

With the advent of *in situ* particle characterization technology, such as FBRM® and PVM®, one can quickly measure the particle phase behavior *in situ* without pulling samples. This paper reviews the implementation of FBRM® and PVM® in the following applications:

- Understanding asphaltene precipitation and deposition in crude oil
- Visualizing gas hydrate formation to ensure consistent flow rates

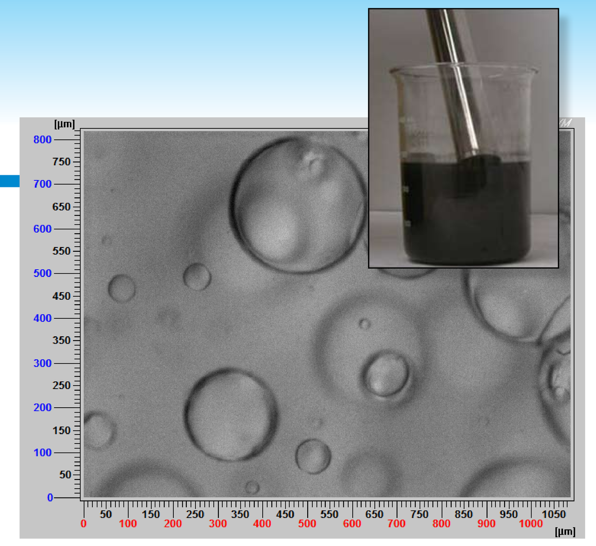


Figure 1. (left) PVM® image of 5 wt% water droplets in a continuous crude oil phase.

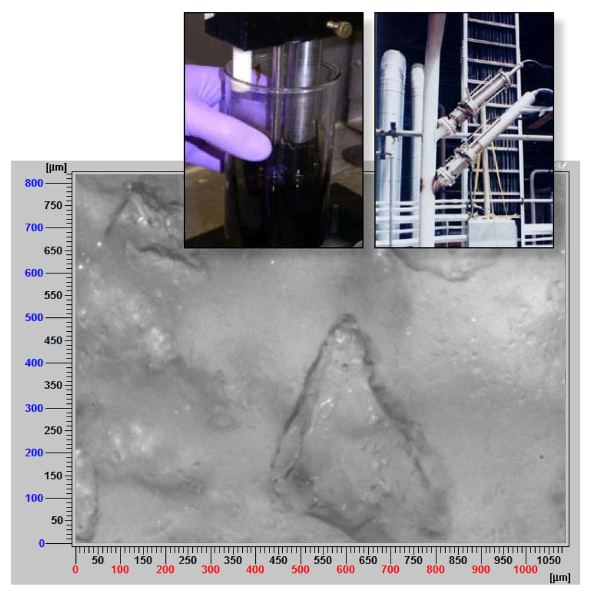


Figure 2. (right) PVM® image of hydrate crystals in a continuous crude oil phase.

Introduction to In-Process Particle Charcterization Technology

PVM® is a probe-based video microscope that provides high quality images of particles and droplets as they naturally exist in process. The size, shape, and structure of particles, droplets and bubbles is immediately revealed allowing petrochemical scientists and engineers to make better and faster decisions regarding the optimization of flow assurance and separation processes.

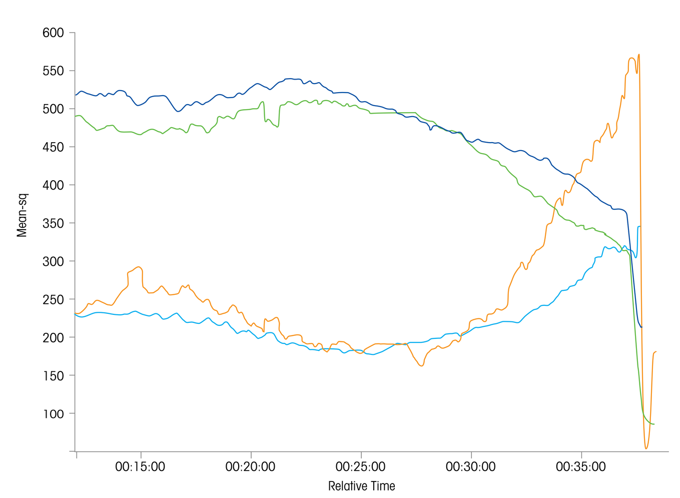


Figure 3. FBRM® identifies and quantifies particle agglomeration or droplet coalescence in real time.

FBRM® tracks the rate and degree of change to particles and droplets as they naturally exist in process. In real time, FBRM® provides critical, previously unattainable information by showing how process variables, such as temperature, pressure, additive concentration or shear rate impact particle and droplet population and dimension. In this way, petrochemical scientists and engineers use FBRM® to control the particle and droplet distribution to guarantee optimal flow and optimize separation efficiency.

Case Study 1: Understanding Hydrate Formation Mechanisms

COLORADO SCHOOL OF MINES

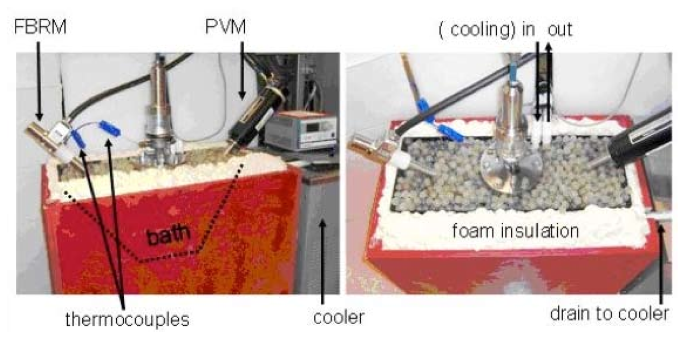
Chevron

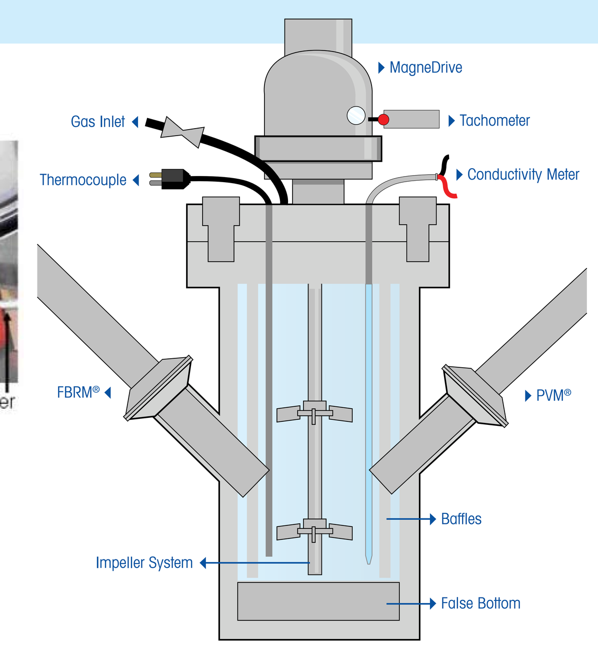
Experiments

- Conroe crude oil in water
- Hydrate Formation
  T = 4°C; P = 77bar
- Hydrate Dissociation T = 20°C

Goal

- Oil production from older/less profitable wells usually have higher water cuts
- Inhibitor addition typically proportional to water cut – can be very expensive
- Study aims to increase understanding of hydrate formation/ dissociation at high water cuts - >60 vol% water





- Hydrate formation typically depends on feed composition, temperature and pressure
- Suitable conditions regularly occur in pipelines – deep sea or arctic regions
- Thermodynamic inhibition of hydrates is possible, but expensive
- Droplet population and dimension impacts the rate and degree of hydrate formation
- Sampling and offline analysis is limited by high pressure and difficult sample preparation
- In-process FBRM® and PVM® are used to understand, monitor, and control hydrate formation/agglomeration - ensuring consistent flow and avoiding plugging

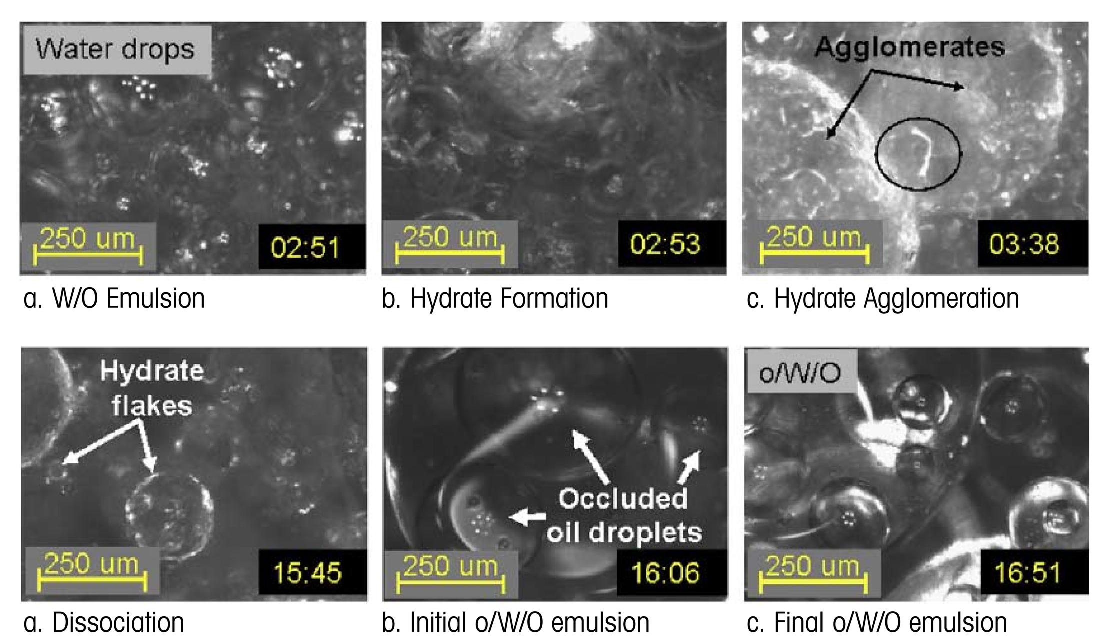


Figure 7.

In-Process PVM® Experiments

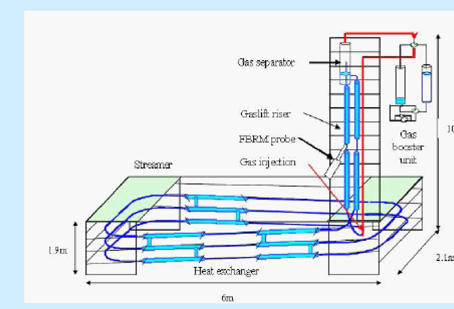
- Hydrate formation/dissociation decreases the emulsion formulation in favor of W/O emulsions – possibly due to hydrate flakes changing water chemistry.
- Previously it was thought that for O/W emulsions hydrate formation would result in catastrophic conversion to W/O emulsions.
- This work showed this not to be the case, possibly because the oil is trapped in the hydrate shell.
- For W/O emulsions hydrate formation leads to rapid agglomeration leading to large water droplets or potentially a free water phase.

In-Process FBRM® Experiments

- The initial droplet distribution impacts the degree of hydrate agglomeration.
- It is possible to correlate the rate and degree of water conversion to initial droplet distribution.

Case Study 2: Monitoring Hydrate Formation in Pipeline Flow

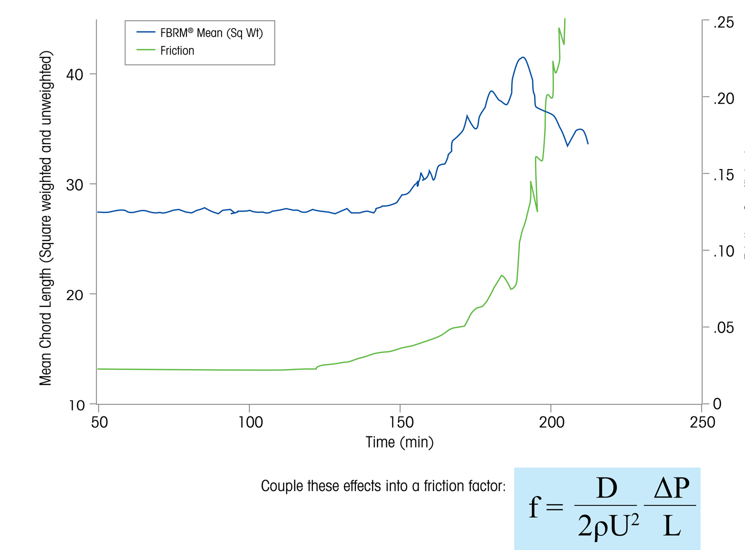
ifp TOTAL



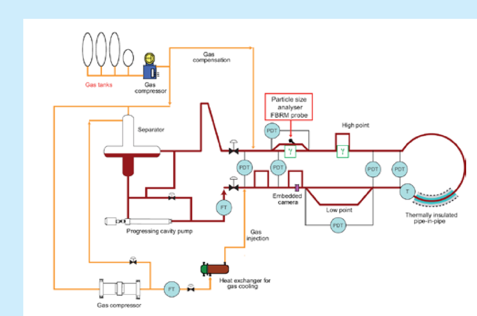
Archimedes Loop

- Temperature controlled (273-283°K)
- No pumps - avoid hydrate crushing
- Gas lift regulates flow
- 36.1m length
- 1.02m internal diameter

- Increase in FBRM® mean correlates to increase in friction factor
- FBRM® used to directly monitor the rate and degree of agglomeration
- FBRM® identifies conditions under which rapid agglomeration and plugging is probable

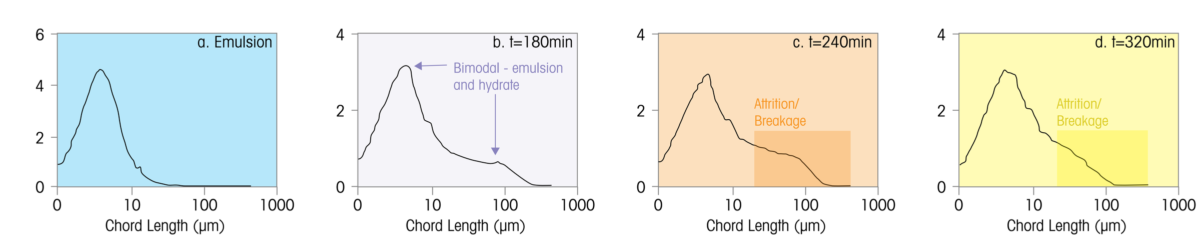


$$f = \frac{D}{2\rho U^2}\frac{\Delta P}{L}$$

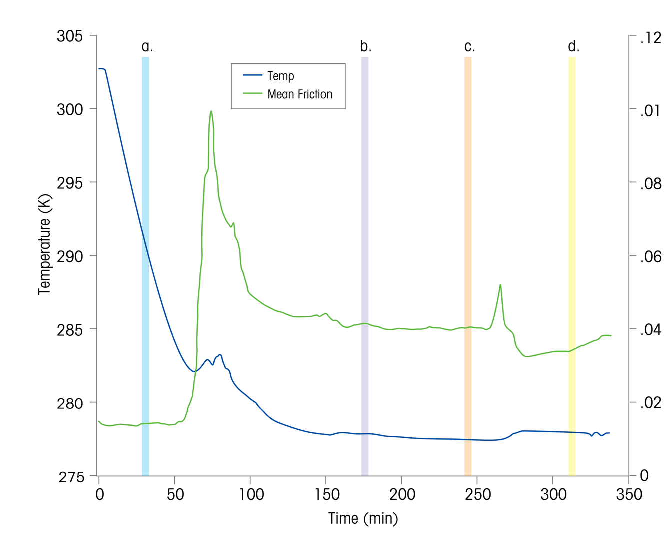


Lyre Loop

- Temperature controlled (273-323°K)
- Moineau pump regulates flow
- Flow constant at different viscosities
- 140m length
- 4.73cm internal diameter



- Initial emulsion distribution – unimodal
- After hydrate formation – bimodal
- In the Lyre Loop mean velocity is kept constant resulting in high shear
- FBRM® tracks rate and degree of hydrate breakage/attrition

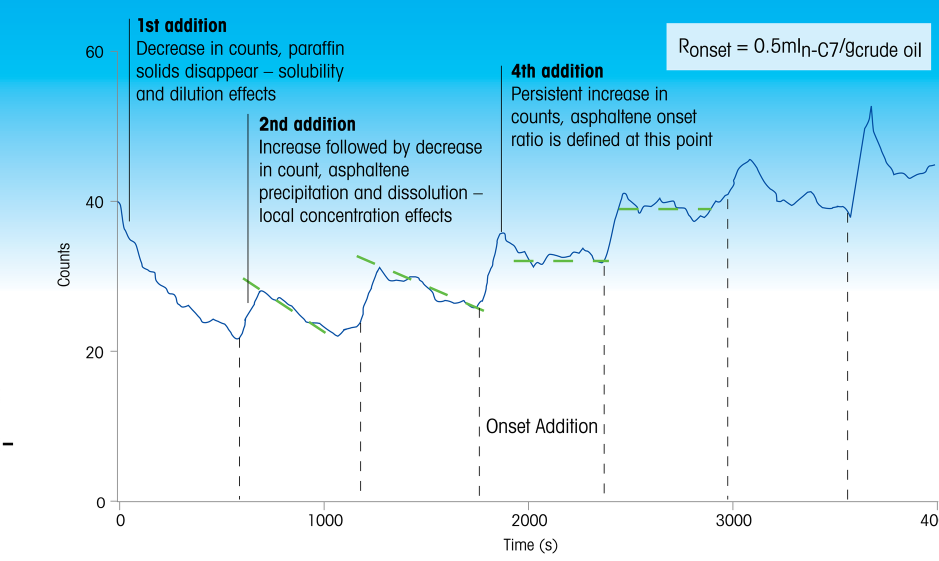


Case Study 3: Understanding Asphaltene Precipitation Mechanisms

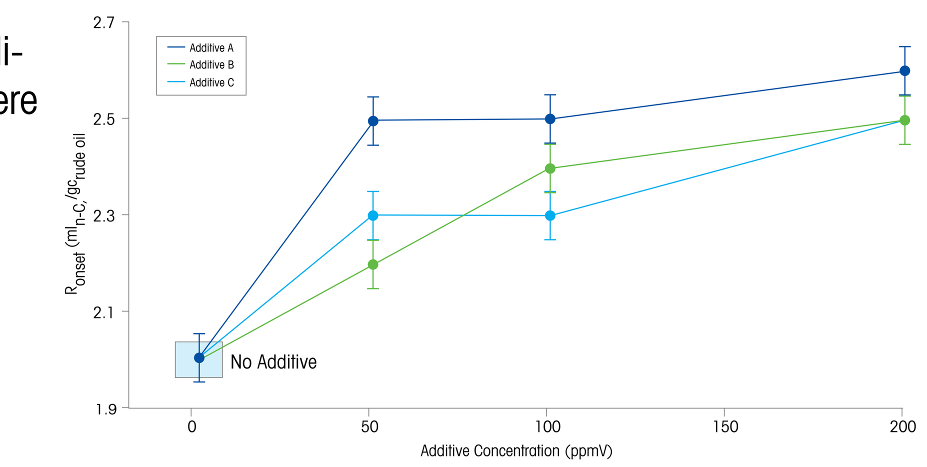
Universidad Rey Juan Carlos

REPSOL YPF

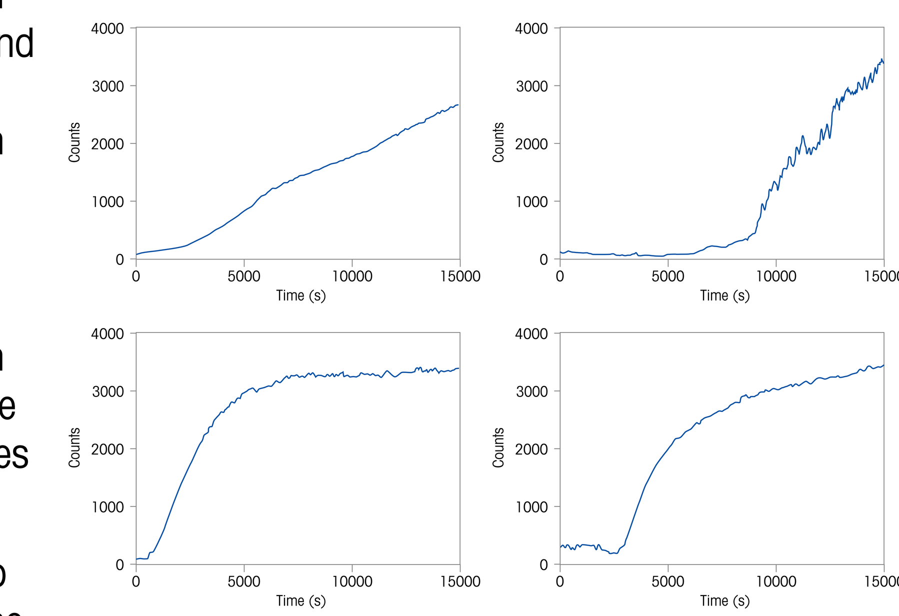
- Onset ratio and asphaltene precipitations kinetics are studied for four crude oils and a 190+ residue
- 40g of crude oil is placed in a glass beaker and agitated at 400rpm
- FBRM® is used to track the rate and degree of change to particle count and dimension in-process and in real time



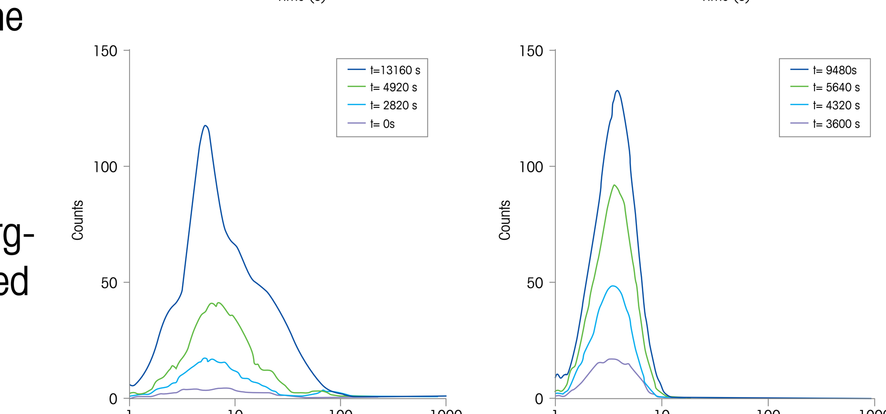
- FBRM® rapidly determines the onset ratio for different crude oils - with no sampling required



- Three commercial additives - A, B and C - were added to the D-190+ residue at different ppmV concentrations



- FBRM® was used to quickly screen the most suitable additive type and concentration to inhibit asphaltene precipitation
- By studying these kinetic effects - we can understand and control asphaltene precipitation and deposition for crude oils from various sources
- FBRM® distributions also provide insight into differences in asphaltene dimension
- For example the asphaltenes precipitated from Crude Oil A are larger than those precipitated from Crude Oil D



Conclusions

METTLER TOLEDO FBRM® and PVM® enable petrochemical scientists and engineers to understand, characterize and control particle droplet and particle formation in complex multiphase pipeline flow. By using METTLER TOLEDO in-process particle characterization tools:

- Mechanisms of hydrate formation can be quickly understood and characterized under a range of process conditions.
- FBRM® measurements can be directly correlated to process parameters (friction factor) that can predict pipeline plugging.
- FBRM® was used to quickly screen the most suitable additive type and concentration to inhibit asphaltene precipitation.

References

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